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Catalytic Synthesis of Carbonated Soybean Oil

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Abstract Carbonated soybean oil (CSBO) can be used as intermediate for the synthesis of non-isocyanate polyurethanes (NIPUs). In this work, CSBO was prepared by the reaction of epoxidized soybean oil (ESBO) with carbon dioxide (CO_2) using a novel composite catalyst comprising $SnCl_4 \cdot 5H_2O$ and tetrabutylammonium bromide (TBABr). The evolution of the reaction process and structure of CSBO were studied by means of IR, ^{1}H-NMR, and GPC techniques. Effects of catalyst formulation and various reaction conditions on the reaction were examined. The results showed that the obvious improvement in ESBO conversion using the present composite catalyst under mild conditions was achieved. Moreover, it was interesting to note that very high purity of CSBO was not a prerequisite for the synthesis of NIPUs with good performance.

Keywords Carbonated soybean oil · Renewable resource · Catalyst · Non-isocyanate · Polyurethanes

1 Introduction

Polyurethanes are a class of important commodity chemicals with broad spectrum of applications. Commercially, polyurethanes are produced by the polyaddition of isocyanates and polyols. The process is problematical in that it has to use toxic isocyanates which are manufactured from even more dangerous phosgene. Moreover, the starting materials used mainly rely on the petrochemical origin. With the shortage of global petroleum supply and increasing environmental concerns, utilization of the renewable resources and complete obviation of the need for isocyanates to synthesize polyurethanes are highly desirable.

Among the various renewable resources, epoxidized soybean oil (ESBO) and carbon dioxide (CO_2) deserve special attention. Apart from the low price and ready availability, ESBO contains active oxirane moieties in its molecule, which renders it with the energy for some reactions [1–2]. Until now, ESBO is primarily used as plasticizers for polyvinyl chloride, chlorinated rubber and polyvinyl emulsions to improve their stability and flexibility [3]. In addition, some efforts have focused on the conversion of ESBO into polyols for use in the polyurethane industry [4–7].

Recently, the CO_2 mitigation and fixation has received much attention because CO_2 is the major greenhouse gas causing global warming and the most inexpensive C1 building block [8]. The production of useful chemicals from CO_2 not only has economic incentive, but also renders positive impact on global environment. In particular, the cycloaddition of CO_2 into small epoxides such as propylene oxide (PO) and ethylene oxide (EO) to afford five-membered cyclic carbonate with versatile reactivity and the subsequent reaction between the cyclic carbonate

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and aliphatic primary amine forming urethane linkage have been the active subjects of investigations since they allow non-isocyanate polyurethanes (NIPUs) to be prepared [9–12].

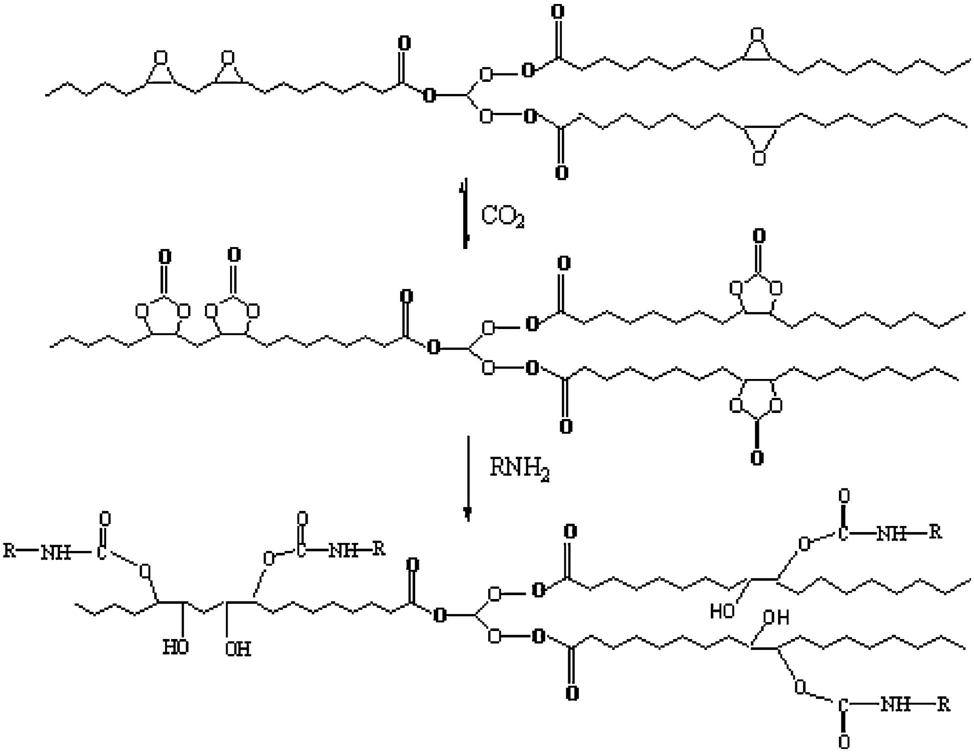
Upgrading of ESBO to value-added NIPUs through the coupling with CO_2, followed by the reaction with amine has also attracted more attention in terms of green chemistry and sustainable development of polyurethane industry. As illustrated in Scheme 1, this process is composed of following two stages [13–16]: ESBO reacts first with CO_2 in the presence of catalyst yielding CSBO, and then CSBO formed reacts further with primary amine to give aimed products. In this process, synthesis of CSBO is a crucial step. Although cycloaddition of CO_2 to small epoxides (PO or EO) towards five-membered cyclic carbonates has made great achievement, transformation of ESBO into CSBO with higher conversion is not an easy task because the limited oxirane groups in ESBO molecule are located in the middle of the molecule chain rather than in terminal position. It can be reasonably conceived that the reactivity of these epoxy groups to CO_2 is lower than that of EO or PO due to the steric hindrance. Several studies in this field have been reported in open literatures. However, they are plagued by a number of drawbacks. For example, Wilkes and co-workers used tetrabutylammonium bromide (TBABr) as catalyst to conduct the reaction and achieved a conversion of 94% after 70 h [17–18]. So long reaction duration may constitute an obstacle for its commercial application in the future. Most recently, Doll et al. reduced the reaction time by 1/3 using supercritical carbon dioxide and 100% conversion of ESBO into CSBO was obtained after 40 h [19]. However, the rigorous operating condition is energy-consuming and potentially dangerous. In addition, Parzuchowski et al. reported the synthesis of CSBO using KI coupled with 18-crown -6 as catalyst under 6 MPa for a couple of days [20]. The expensive catalyst along with long reaction time could make it economically unfavorable. It appears that more efforts are needed to consummate this synthetic process.

In this work, a new binary catalyst system comprising $SnCl_4 \cdot 5H_2O$ and TBABr was applied to the carbonation of ESBO with CO_2. The evolution of the process and the structures of CSBO were investigated by IR, ^{1}H-NMR, and GPC techniques. Moreover, the effect of CSBO content in resultant carbonation product on the mechanical properties of NIPU materials was also investigated.

2 Experimental

2.1 Materials

ESBO with a molecular weight of ca. 1,000 g/mol and 4.2 epoxy groups per triglyceride was obtained from Shanxi Chemical Factory, China. Carbon dioxide (99.999%) was purchased from Beijing Beiwen Gases Company, China.



Scheme 1 Cycloaddition of carbon dioxide into ESBO and subsequently aminolysis of CSBO with primary amines

Tetrabutylammonium bromide (TBAB), Stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), and ethylenediamine (EDA) were analytical grade reagents purchased from Sinopharm Chemical Reagent CO., China. They were used as received without further treatment.

2.2 Preparation of CSBO

ESBO (85 g) and various catalysts (3 mol% with respect to epoxy groups) dissolved in DMF were charged into a 100 mL stainless steel autoclave equipped with gas inlet tube and outlet, thermometer, and mechanical stirrer. After leak test and purging with CO_2, the reactor was heated under stirring. When the desired reaction temperature was reached, the reaction mixture was pressured with CO_2 to a definite value, and kept for different time. At the end of reaction, unreacted CO_2 was vented out. The catalyst was completely removed by dissolving in ethyl acetate and washing the reaction mixture twice with hot water. The organic layer was then distilled off under reduced pressure. A series of clear, light-brown products was obtained.

The content of carbonate groups in product was calculated by a titration method described in literature [20].

2.3 Preparation of NIPUs

The NIPUs were prepared by mixing CSBO products obtained above with ethylenediamine (EDA) as hardener at 60–80 °C for 2–5 min. The viscous mixtures produced were then poured into a mold of 180 mm × 180 mm × 2 mm. The curing reaction was carried out at 90–100 °C for 20–30 h in an oven to give light-brown, transparent sheets. The sheets were further aged at room temperature for 7 days.

2.4 Measurements and Characterization

FT-IR spectra were collected on a Nicolet 380 spectrometer. ^{1}H-NMR spectra were recorded on a DRX 300 (300 MHz) spectrophotometer using tetramethylsilane as an internal standard. GPC chromatograms were obtained on a SHIMADZU RID-10A equipped with RI detector using DMF as the eluent. Viscosity measurement was performed on a NDJ-1 rotational viscometer at 25 °C. Tensile strength, tensile modulus at 100% elongation, elongation at break, and tear strength measurements were measured at ambient temperature on an Instron 4201 instrument. Rebound measurement was performed on an Instron 4221 rubber impacting elasticing tester. Hardness (Shore A) measurement was carried out on a sclerometer.

3 Results and Discussion

3.1 Synthesis of CSBO

In our laboratory, development of the composite catalyst consisting of Lewis acid and Lewis base for this purpose has been one of the emphases due to its unique performance. In this work, a new catalyst system comprising TBABr and $SnCl_4 \cdot 5H_2O$ was used and the results were presented in Table 1.

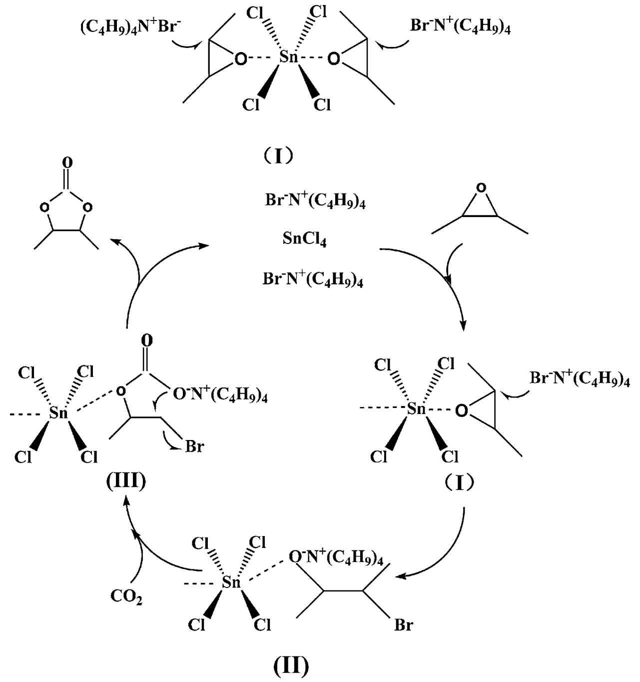
It was observed from the table that although the separate TBABr and $SnCl_4 \cdot 5H_2O$ had lower catalytic activity for this reaction (ESBO conversion of 71.3% and 64.4%, respectively), the combination of them with different molar ratios resulted in a dissimilar improvement in ESBO conversion under the identical reaction conditions. The activity of these catalysts increased in following order: $SnCl_4{\cdot}5H_2O$/TBABr (2:1) < $SnCl_4 \cdot 5H_2O$/TBABr (1.5:1.5) < $SnCl_4 \cdot 5H_2O$/TBABr (1:5) < $SnCl_4 \cdot 5H_2O$/TBABr (1:2) < $SnCl_4 \cdot 5H_2O$/TBABr (1:4) < $SnCl_4 \cdot 5H_2O$/TBABr (1:3). In particular, ESBO conversion of 89.2% was reached when the ratio was 1:3. Because the total mole fraction of the catalyst for each run maintained constant, the results in Table 1 implied that a synergic effect between TBABr and $SnCl_4 \cdot 5H_2O$ might occur. The reason for this is that the function of Lewis base is to activate CO_2, while Lewis acid is to activate epoxy groups in ESBO. The union of these two sites may constitute a co-function effect to promote the reaction more efficiently than either the separate TBABr or $SnCl_4$. As a consequence, higher conversion of ESBO is realized. A possible reaction pathway which is similar to the coupling reaction between CO_2 and styrene oxide [21–24] was proposed as illustrated in Scheme 2. An explanation is given below.

Two epoxy groups in ESBO is first activated by the coordination with one Lewis acid site Sn, forming complex (I); As a stronger nucleophilic reagent, Br^- anion in TBABs

Table 1 Effects of catalyst composition on the conversion of ESBO

Entry	Catalyst (3 mol%)	Conversion (%)
1	TBABr	71.3
2	$SnCl_4 \cdot 5H_2O$	64.4
3	$SnCl_4 \cdot 5H_2O$/TBABr (1:5)	84.7
4	$SnCl_4 \cdot 5H_2O$/TBABr (1:4)	87.4
5	$SnCl_4 \cdot 5H_2O$/TBABr (1:3)	89.2
6	$SnCl_4 \cdot 5H_2O$/TBABr (1:2)	85.8
7	$SnCl_4 \cdot 5H_2O$/TBABr (1.5:1.5)	81.1
8	$SnCl_4 \cdot 5H_2O$/TBABr (2:1)	79.0

Reaction conditions: temperature: 120 °C, CO_2 pressure: 1.0 MPa, reaction time 20 h



Scheme 2 Possible reaction pathway for CSBO formation

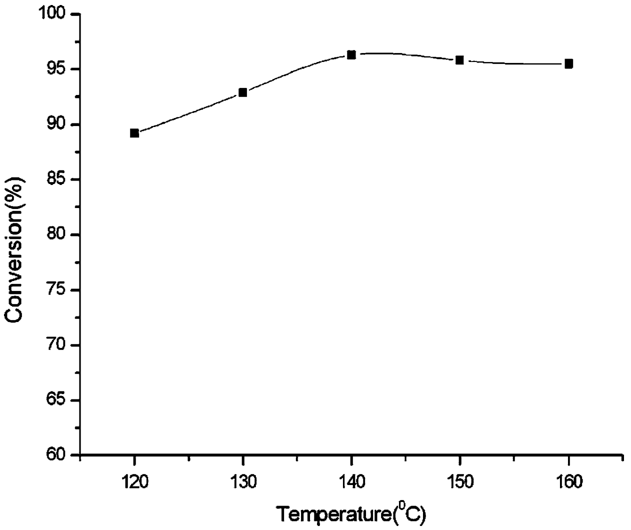


Fig. 1 Reaction temperature dependence of ESBO conversion. Reaction condition: CO_2 pressure: 1.0 MPa; reaction time: 20 h; catalyst: $SnCl_4 \cdot 5H_2O$/TBABr (1:3)

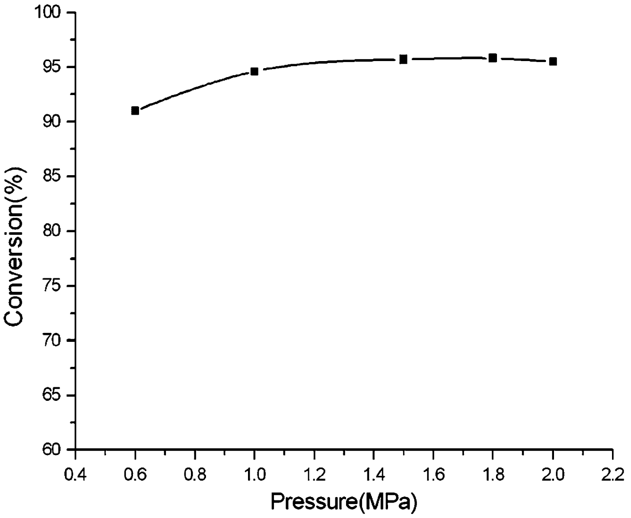


Fig. 2 CO_2 pressure dependence of ESBO conversion. Reaction condition: temperature 140 °C; reaction time: 20 h, catalyst: $SnCl_4 \cdot 5H_2O$/TBABr(1:3)

then attacks carbon atom of complex (I), followed by ring opening, generating an oxy anion species (II). The insertion of CO_2 into the Sn–O bond of (II) would give a Sn-carbonate intermediate species (III), which finally provides the cyclic carbonate group. During this process, two epoxy groups may be coordinated with one $SnCl_4 \cdot 5H_2O$ molecule and two Bu_4NBr molecules interact with complex (I). This well explained the requirement of coexistence of $SnCl_4 \cdot 5H_2O$ and *n*-Bu_4NBr to achieve optimum catalytic efficiency.

Figure 1 shows the temperature dependence of ESBO conversion. It was found the ESBO conversion increased with temperature up to 140 °C, and reached maximum (94.1%) at this point. The conversion then decreased lightly with further increase of temperature. This is easily understood. On the one hand, the kinetic reaction rate increases with temperature. On the other hand, carbonation of ESBO is an exothermic reaction and too high temperature may shift the equilibrium to the left. The trade-off between kinetic and thermodynamic factors leads to the best reaction performance observed at 140 °C. It suggests that temperature is an important option to implement the desirable ESBO conversion.

Figure 2 shows the CO_2 pressure dependence of ESBO conversion for the same catalyst at 140 °C. It can be observed that the ESBO conversion increased with pressure below 1.5 MPa, and maintained constant at 1.5 MPa and above. The reasons for these may be as follows: In general, higher pressure favors the reaction of CSBO formation as it is the reaction of volume reduction. However, the increase of pressure from 1.5 MPa to 2.0 MPa is helpless to further promote the interaction between ESBO and catalyst, and to further enhance the ESBO concentration in the reaction system. In other words, the effect of pressure variation in such range on ESBO conversion is quite limited.

Table 2 shows the reaction time dependence of conversion, viscosity and molecular weight. It can be seen that with prolonging the reaction time, the ESBO conversion increased steadily, and reached 98.6% after 40 h. Meanwhile, the viscosity of product increased correspondingly.

Table 2 Reaction results of carbonation of ESBO

Reaction time (h)	Conversion (%)	Viscosity (cp s)	Mw
0	0	420	1,018
10	86.9	11,290	1,292
20	95.5	16,440	1,390
30	98.6	19,320	1,409

Reaction conditions: temperature: 140 °C, CO_2 pressure: 1.5 MPa, catalyst:$SnCl_4 \cdot 5H_2O$/TBABr(1:3)

At the end of reaction, the value reached 19,320 cp, almost 40-fold as large as of ESBO. The change of viscosity may be related to the change of the product structure. Taking into account the unconspicuous discrepancy in molecular weight of products, the increase of viscosity should be ascribed to the enhanced intermolecular interactions caused by the formation of highly polar cyclic carbonate groups instead of the polymerization of ESBO [17–20].

The transformation of ESBO to CSBO was traced by IR spectroscopy and ^{1}H-NMR spectroscopy as shown in Fig. 3(a, b) and Fig. 4, respectively. Compared with curve (a) in Fig. 3, curve (b) showed following characteristics: two peaks at 845 and 823 cm^{-1} corresponding to epoxy absorption disappeared, while a new band at 1,805 cm^{-1} due to the carbonyl of the cyclic carbonate moieties appeared. This confirmed that the ESBO was converted into CSBO availably.

As additional evidence, results of ^{1}H-NMR spectroscopy corroborated this conclusion. It was clear from Fig. 4 that original epoxy groups $\delta = 2.80$–3.20 ppm disappeared after the reaction of ESBO with CO_2, while new cyclic carbonate groups had emerged at $\delta = 4.45$–4.90 ppm.

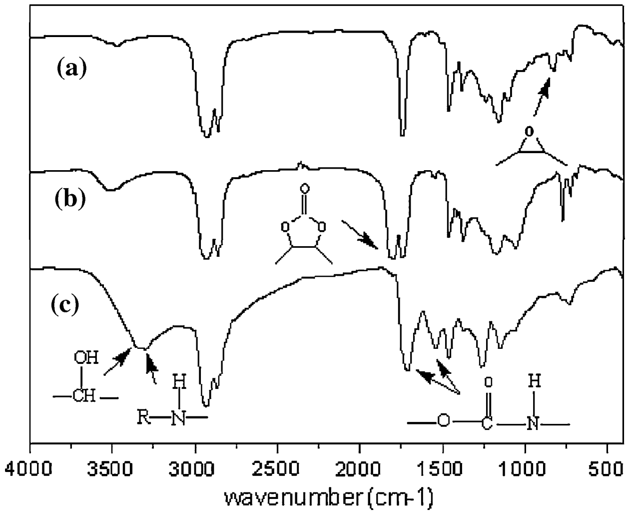


Fig. 3 Typical IR spectra of ESBO (**a**), CSBO (**b**) and NIPU (**c**)

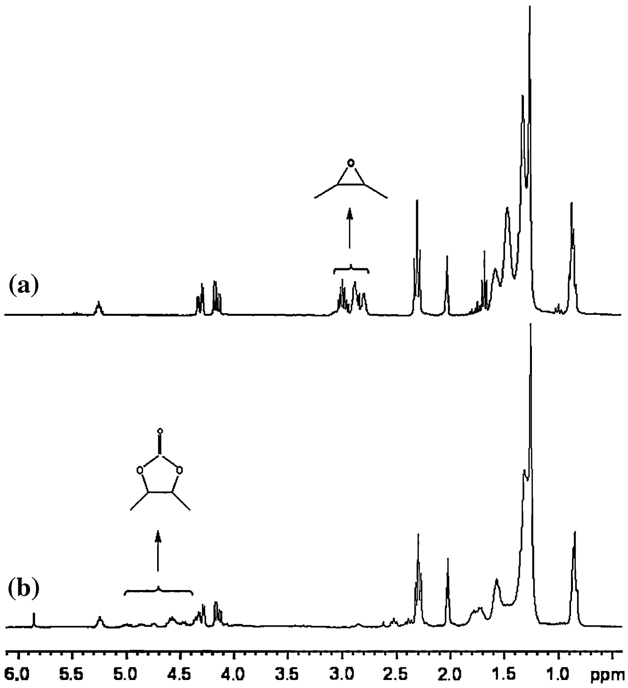


Fig. 4 ^{1}H-NMR spectra of (**a**) ESBO and (**b**) CSBO

3.2 Synthesis of NIPUs

The reaction between CSBO and EDA as the hardener was monitored using IR spectroscopy through inspecting the disappearance of band at 1,805 cm^{-1} and appearance of new bands at 1710, 1540, and 3337 cm^{-1} as shown in Fig. 3(c). According to the literature, they were assigned to carbonyl absorptions in urethane groups, N–H deformation of the urethane group, and hydroxyl groups, respectively [17]. It was observed that with the progress of reaction, the peak at 1,805 cm^{-1} corresponding to the cyclic carbonate moieties continuously attenuated while the new bands synchronously strengthened. This indicated that the β-hydroxyurethane linkages were generated via the reaction of CBSO and amine.

3.3 Mechanical Properties of NIPU Material

A series of NIPU samples was elaborated via the reaction of CSBO products above at different conversions with EDA. The representative results with respect to the mechanical properties of these samples were shown in Table 3. It can be seen that all of the mechanical properties, except for elongation at break, were enhanced initially and then decreased with the increase of the conversion, while the elongation at break behaved in an opposite way. It was interestingly discovered that the ESBO conversion corresponding to the optimal properties was not 100% but

Table 3 Effects of ESBO conversion on mechanical properties

Conversion (%)	55.4	74.3	85.1	90.9
Hardness (Shore A)	85	93	92	84
Rebound (%)	8	14	12	9
Elongation at break (%)	232	173	163	207
Tensile strength (MPa)	2.63	7.0	6.9	4.56
Tensile modulus at 100% elongation (MPa)	1.19	4.8	5.2	2.3
Tear strength (KN/m)	11.2	30.6	27.8	18.6

in a range from 74.3% to 85.1%. When the conversion was lower than ca. 74.3%, the resultant NIPUs were generally slabby and their mechanical properties were inferior. This is probable that the lower conversion results in the less hydroxyurethane linkages and weaker intermolecular interaction. On the contrary, if the ESBO conversion was greater than ca. 85.1%, the mechanical properties of resulting NIPU were also degraded. It is very likely that existence of overfull cyclic carbonate groups is unfavorable for the sufficient reaction with amine owing to the steric hindrance of these groups. In this case, overfull, unreacted amine acts as a plasticizer, leading to poor mechanical properties. Somewhat analogous finding was reported in the literature for the preparation of so-called hybrid non-isocyante urethane networks (HNIUNs) using cyclocarbonate oligomer and amine oligomer, the authors claimed that an optimum in mechanical properties (tensile strength, ultimate elongation) related to the existence of terminal epoxy groups with certain amount in starting material. A range of 4–12% epoxy relative to cyclic carbonate provided the best performance [15]. Apart from the difference in starting materials, both cyclocarbonate groups and epoxy groups are located in the middle of molecular chains rather than in terminal position in the present work.

Because the conversion level of ESBO reflects the CSBO content in carbonated product, present results clearly demonstrated that very high CSBO content (ESBO conversion) is not essential for the preparation of NIPUs with good mechanical properties. In other words, the presence of proper amount of unconverted oxirane groups in CSBO product is advantageous than pure CSBO. Therefore, reaction conditions such as temperature, pressure, and time on stream in carbonation process could be further optimized. From the view of point of energy-saving, this is of significant importance.

4 Conclusions

A new, effective composite catalyst composed of $SnCl_4$ $5H_2O$ and TBABr for the synthesis of CSBO from ESBO and CO_2 was presented in this paper. The investigation on catalyst formulation indicated that $SnCl_4 \cdot 5H_2O$/TBABr catalyst with 1:3 molar ratio exhibited the best performance among the catalysts used in this work. The reason for this was given based on a possible reaction pathway. Effects of various reaction conditions including reaction temperature, CO_2 pressure, and time on stream on the reaction were examined. Moreover, this work revealed that very high purity of CSBO was not a prerequisite for obtaining NIPUs with good performance. This will make it possible to implement CSBO synthesis under mild conditions.

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